UNIVERSITAT ROVIRA I VIRGILI

Theoretical Study of the Basicity and the Redox Properties of Heteropolyanions

Xavier López Fernández

Departament de Química Física i Inorgànica

Memòria presentada per optar al títol de Doctor en Química

UNIVERSITAT ROVIRA I VIRGILI

El Dr. Josep Maria Poblet Rius, Catedràtic de Química Física, i el Dr. Carles Bo Jané, Professor Titular de Química Física del Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili

Fem constar que la present memòria, que porta per títol:

"**Theoretical Study of the Basicity and the Redox Properties of Heteropolyanions**",

ha estat realitzada sota la nostra direcció al Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili pel llicenciat en química Xavier López Fernández per obtenir el grau de Doctor en Química.

Tarragona, 10 de Juliol de 2003

Dr. Josep Maria Poblet Rius

Dr. Carles Bo Jané

Preface

This thesis aims to provide valuable information to the community concerned with transition-metal coordination chemistry in general, and high nuclearity molecular metal oxides in particular. Experimental data on polyoxometalates (POMs) has been available for more than 150 years, when Berzelius, Marignac and others first started to study this new field in chemistry. Since then, countless POM compounds have been characterised. This family of molecules is appealing for scientists from an academic point of view but they have also proved to have some very interesting value-adding features that can be used for technological purposes. For example, they can selectively encapsulate ionic species and catalyse many organic reactions and they are environmentally-friendly wood pulp bleachers, membranes, sensors, etc. In the future, they may be successfully applied to medicine because they are now being tested as antiviral agents. The list of possible applications is endless. Be that as it may, many groups are working to exploit the properties of these metal oxides. Therefore, accurate knowledge of the fundamental properties of POMs is required if experimentalists are to develop new technologies.

Theoretical chemists started to make a contribution just a few decades ago with the routine use of computers. When I began this PhD. thesis in 1999, first-principles theoretical studies on POMs were really scarce. They were limited to a few articles published by the groups of Marc Bénard, Serguei A. Borshch and Josep M. Poblet. Nevertheless, they laid the basis for further investigation in the field of POMs. This book, entitled "*Theoretical Study of the Basicity and the Redox Properties of Heteropolyanions*", summarises the work I have done in the last four years on the general properties of the two title clusters. The development of increasingly efficient software, together with the increasing power of computers, enables computational chemists to play an important role in science. Nowadays, the accuracy of some calculations depends on the instruments used in the laboratory. It goes without saying that the information provided by high-performance calculations is essential if we are to have the complete picture of a chemical problem. For the time being, the data provided by theoreticians can corroborate or explain experimental observations. The ultimate goal of computational chemistry is to have a true predictive role.

This thesis is structured in two main parts. Part I introduced the work. Chapter 1 is an overview to the field of polyoxometalates and provides basic information about their structure and principal properties. Chapter 2 deals with the first-principles method of calculation used throughout this work, the density functional theory. It also describes the fundamentals of the methodology, computational details and some useful analytical tools. The last chapter in this section discusses the theoretical studies that have been made on POMs to date. Part II presents and discusses the results arising from this PhD, and is structured in five chapters. The first two describe the electronic properties and the α/β-isomerism of single-addenda clusters. They also discuss the redox properties of their mixed-addenda partners. The third block (chapter 6) deals with the basicity of the oxygen atoms in these anions and the study of the dimerisation reaction in some Keggin clusters. Chapter 7 is a study of a mixed-metal Mo/V cluster which was found to have special electronic properties. Finally, chapter 8 discusses two methodologies applied in the field of computational chemistry. They are aimed at including the effects of the environment to molecules.

While working on this PhD. thesis —some parts in collaboration with other groups— I have had six articles published in international journals or recently accepted for publication. Three manuscripts are in preparation.

Tarragona, July 2003

Table of Contents

PART II. RESULTS

A la meva família i amics

Nothing exists but atoms and empty space. All the rest are opinions

No existeix res més que àtoms i espai buit. La resta són opinions

Demokritos